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# Effect of Overstretched Polymer Chains on Shear-Thickening Observed in Associating Polymer Gels

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概要: 会合基を有する高分子を会合高分子と呼ぶ。Gauss 領域を超えて伸張する高分子鎖が、会合高分子ゲルの非線形粘度に与える影響を議論する。張力の非線形項が適度に大きい場合は shear-thickening が起こることを示す。しかし鎖の解離率 (鎖の会合基が単位時間当りにネットワーク架橋点から解離する確率) が鎖の張力に敏感に依存する場合は、張力の非線形項が大きくても shear-thickening は起こらないことが示される。

## 1 Introduction

Shear-thickening phenomenon, or a growth of nonlinear viscosity with shear rate, is one of the characteristic rheological behavior observed in aqueous solutions of associating polymers. Despite many studies from both experimental and theoretical sides, molecular origin of shear-thickening behavior remains unclarified. We theoretically analyze shear-thickening on the basis of transient network theory[1] from the viewpoint of the overstretching effect of polymer chains beyond the Gaussian regime along the shear flow.[2]

## 2 Model

In order to examine the effect of overstretched polymer chains beyond the linear regime on the nonlinear viscosity, we adopt the chain tension given by the form

$$\tau(r/l) \equiv \frac{f(r)a}{k_B T} = 3 \frac{r}{l} \left( 1 + \frac{2A}{3} \frac{(r/l)^2}{1 - (r/l)^2} \right), \quad (1)$$

where  $f(r)$  is the tension along the chain having end-to-end length  $r$ ,  $a$  is the monomer length,  $l$  is the contour length of the chain ( $k_B$  is the Boltzmann constant and  $T$  is the temperature). Overstretching effect of the chain appears when its end-to-end length elongates longer than  $\sim l/(1+A)^{1/2}$ . As the chain stretches longer along the flow, the possibility that the associative groups at chain ends dissociate from network junctions becomes higher due to higher tension of the chain. We assume that such dissociation rate is given by

$$\beta = \beta_0(1 + g\tau^2), \quad (2)$$

where the coupling constant  $g$  gives the measure of how sensitively the dissociation rate is influenced by the tension.

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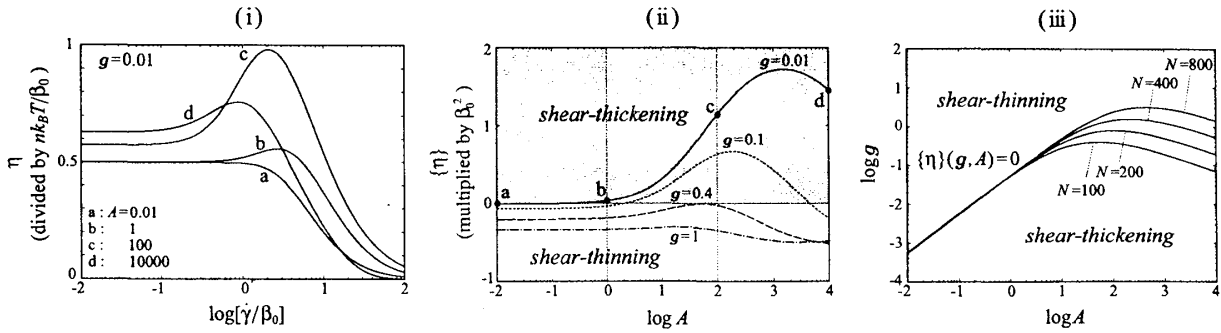


Figure 1: (i) The nonlinear viscosity plotted against the shear rate. The amplitude  $A$  in the tension varies from curve to curve (corresponding to a,b,c,d in (ii)) for fixed  $g(=0.01)$  and the number  $N(=100)$  of segments. (ii) The nonlinear intrinsic viscosity coefficient  $\{\eta\}$  plotted against  $A$ . The coupling constant  $g$  is varied from curve to curve for fixed  $N(=100)$ . (iii) The thickening phase diagram. The region below each curve given by  $\eta(\beta_1, A)=0$  leads to thickening, whereas the region above the curve causes thinning for each  $N$ .

### 3 Thickening/Thinning Transition

In Figure 1 (i), we can see the transition from thinning to thickening with increasing  $A$ . To see the detail of thickening/thinning transition, we introduce the *nonlinear intrinsic viscosity coefficient* defined by

$$\{\eta\} \equiv \lim_{\dot{\gamma} \rightarrow 0} \frac{\eta(\dot{\gamma}) - \eta(0)}{\eta(0)\dot{\gamma}^2}. \quad (3)$$

Shear-thickening should occur when  $\{\eta\} > 0$ . When  $\{\eta\} < 0$ , on the contrary, it is highly expected that only shear-thinning should appear. As shown in Figure 1 (ii), thickening/thinning transition occurs for  $g$  below a certain critical value  $g_c(N)$ . ( $g_c(N=100) \simeq 0.4$  as seen in the figure.) When  $g > g_c(N)$ , we do not observe the transition from thinning to thickening because the chain does not overstretch before it dissociates from a junction due to large coupling  $g$  between the chain tension the breakage rate. Thickening/thinning transition is summarized in Figure 1 (iii) which shows the boundary curves defined by  $\{\eta\}(g, A)=0$  separating the thickening region from the thinning region on the  $A$ - $g$  plane. Thus the balance between  $A$  and  $g$  determines the condition for shear-thickening.

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### References

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